HIGH PURITY LPE GaAs FOR FAR INFRARED BLOCKED IMPURITY BAND DETECTORS

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ABSTRACT

GaAs Blocked Impurity Band (BIB) devices are under development in response to the need for photoconductor detectors that operate at wavelength beyond 200µm. GaAs is an excellent choice for this purpose due to its low donor electron binding energy (6meV). To meet the extreme purity requirements of a BIB blocking layer we have constructed a liquid phase epitaxy system dedicated to ultra-pure GaAs crystal growth. Epilayers are grown out of a saturated Ga/GaAs solution contained by a high purity porous graphite crucible. Growth is performed from 800 to 40°C with an H_2 ambient inside a quartz reactor. To ensure high purity epilayers, the crucible is periodically baked out at 1500°C in vacuum (for one to two days) to remove volatile impurities. In the near future, sapphire will be explored as an alternate material for the crucible. To date the highest purity epilayers grown have been found to be of mixed conduction type, with an average net-doping concentration N_d-N_a of $5x10^{11}cm^{-3}$ determined by capacitance-voltage measurements.

INTRODUCTION

Extreme material purity requirements are necessary for the production of high sensitivity, low noise semiconductor BIB detectors. Recent interest in GaAs as a material for this application, due to its low donor electron binding energy (6meV), has sparked research in growth of high purity GaAs. Liquid Phase Epitaxy (LPE) has proven to be the growth technique capable of the highest purity GaAs films of up to hundreds of microns in thickness[1]. Other techniques such as vapor phase epitaxy[2,3] (VPE) can produce very pure material but at much smaller layer thickness than is required for high sensitivity photoconductor production. In LPE, the material desired to be grown as a film is dissolved at elevated temperature into a metal solution, which is isolated from the substrate. Once the solute has been fully dissolved, the solution is transported over the substrate and the temperature lowered, resulting in precipitation of the solute onto the substrate. In the case of the work described here, GaAs is dissolved into high-purity Ga in a graphite crucible. The solution is tipped onto the GaAs substrate via rotation of the crucible. Growth occurs when the temperature is ramped down, causing the reduction of the solubility of GaAs in Ga. Solute that is forced out of solution by the temperature decrease will preferentially accumulate on the GaAs substrate resulting in epitaxial crystal growth. The thermodynamic segregation of impurity atoms into the liquid phase during growth is what gives LPE its inherent purity advantage.

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EXPERIMENT

A series of GaAs films have been grown on both semi-insulating (SI) and conducting GaAs <100> commercial substrates of roughly 1cm^2 in area. The graphite growth crucible was baked for 24 hours at 1500°C in vacuum followed by baking at 800°C in vacuum inside the LPE system prior to growth. The purpose of baking was to remove volatile impurities, such as sulfur and oxygen, which may have been trapped within the graphite. It is believed that the crucible is the major source of the impurity sulfur. High temperature baking helps to diffuse the sulfur to the surface and drive it out. However, we found that not all sulfur can be removed at reasonable baking temperatures and times.

Prior to growth, substrates were etched in concentrated HCl for 30 seconds to remove the native oxide. Crystal growth occurred inside a fused quartz reactor tube surrounded by a tube furnace. Ten grams of 99.999999% pure Ga (GEO Specialty Chemicals, Cleveland, OH) were used as a solvent, with semi-insulating GaAs (etched in concentrated HCL for 30 minutes) as a solute. A constant flow of palladium purified H_2 was provided during growth, which begins at 810°C and proceeds at a cooling rate of 2°C/min. Up to three growth runs are performed using the same Ga+As solution before it is changed for fresh starting materials.

DISCUSSION

Hall effect and resistivity measurements were performed on layers grown on an SI GaAs substrates. The highest purity films that could be measured were found to have N_d-N_a=5x$10^{12}$$cm^{-3}$ and an electron mobility μ_e=185,000 cm^2/V-s at 77K. These are close to the best values reported by Amano et al.[1] and Bauser et al.[4] Contacts were formed by annealing pieces of In-Sn alloy that was pressed onto the layer. The highest purity films however could not be measured this way, most likely because they are not homogeneous but consist of intermixed p- and n-type islands. To circumvent this problem, films were grown on a conducting GaAs substrate ($10^{17}$$cm^{-3}$ Si doped) to fabricate a Schottky diode structure and determine the net impurity concentration via capacitance-voltage measurements. Schottky diodes were formed by the electron beam evaporation of a Pt contact (Figure 1b). Prior to evaporation, the sample was immersed in HCl and $(NH_3)_2S$ solution. Ammonium sulfide is known to passivate interface defects in GaAs Schottky contacts[5]. A Ni/Ge/Au contact was deposited and annealed at 475°C for 30 seconds in Ar. This serves as an ohmic contact to the conducting wafer. Capacitance-Voltage measurements were performed on one such diode (sample 237C) with an epilayer thickness of 50μm (Figure 1a), which was found to be *fully depleted at zero applied bias*. C-V measurements could therefore only be performed with the diode in forward bias. The space charge concentration in a semiconductor diode is related to the square of the measured capacitance. The slope of the $1/C^2$ vs. V curve for a homogeneously doped diode is equal to:

(2) $$\frac{d\left(1/C^2\right)}{dV} = \frac{2}{A^2 \varepsilon_s q N_d}$$

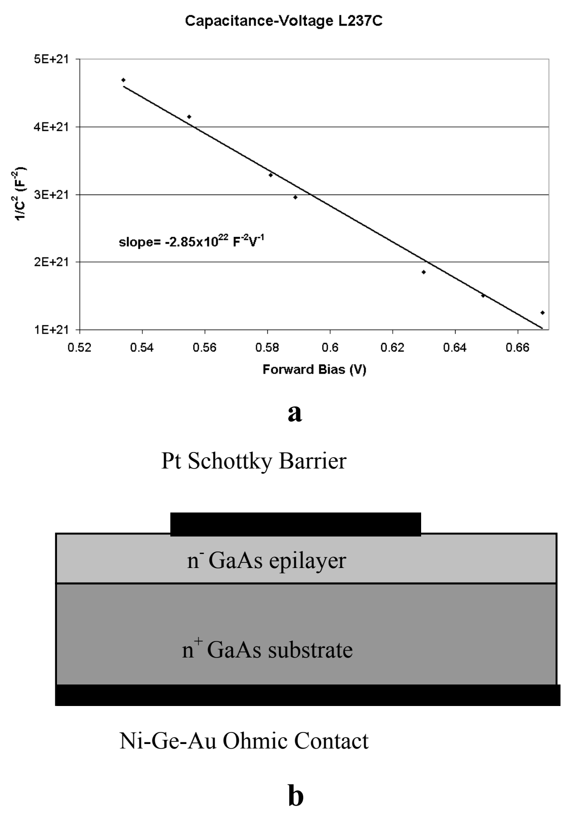

Figure 1: *a) C-V analysis of a GaAs-Pt Schottky Diode b)Cross-section of Schottky Diode used for C-V analysis*

where A is the diode area, ε_s is the dielectric constant of GaAs (12.5 ε_o), and N_d is the net space charge concentration in the n-layer. The slope of the line in Figure 1 was found to be $2.8x10^{22}F^{-2}V^{-1}$, giving a net space charge concentration of roughly $5x10^{11}cm^{-3}$. Low temperature (4.2K) photoluminescence measurements were performed on a sample believed to be of similar purity to 237C (sample 211SI). Exceptionally sharp luminescence peaks indicate that the film is extremely pure (although it may be highly compensated). Figure 2 shows the excitonic region of the spectrum. The neutral donor, acceptor (carbon and zinc), and free exciton peaks are labeled. Magneto-photoluminescence was performed on previously grown samples that were not of as high purity as those under discussion. These measurements revealed that sulfur and silicon were the major donor impurities. The major compensating acceptor was found to be carbon.

High purity GaAs films are crucial to the development of high efficiency, low noise blocked impurity band detectors[6]. Such devices consist of a high purity blocking layer grown on top of a doped infrared active region (Figure 3), which can be doped much more heavily (hence the donor band displayed in Figure 3) than a simple extrinsic photoconductor made from the same material, without concerns over dark current. Only photons absorbed within the depletion region will be able to produce a signal current, so it is necessary to make this region sufficiently broad. The depletion width of a BIB device is determined by the *minority* dopant concentration $N_{minority}$ and the blocking layer thickness b, according to equation 3.

$$w = \sqrt{\frac{2\varepsilon\varepsilon_0 (V_a - V_{bi})}{eN_{minority}} + b^2} - b \tag{3}$$

A BIB fabricated using a film $5x10^{11}cm^{-3}$ minority doping concentration and having a 5μm blocking layer would have a depletion width of 60μm at 1.5V applied bias according to equation 3. The absorption coefficient of GaAs doped at $1x10^{15}cm^{-3}$ for a photon wavenumber of $40cm^{-1}$ has been experimentally determined to be $\alpha=125cm^{-1}$ by Bosomworth et al.[7] If the majority dopant concentration in this film were $1x10^{15}cm^{-3}$, absorption calculations show that 53% of a $40cm^{-1}$ photon flux incident on the detector would be absorbed. This absorption value approaches that of the highest performance Ge far-IR photoconductors available.

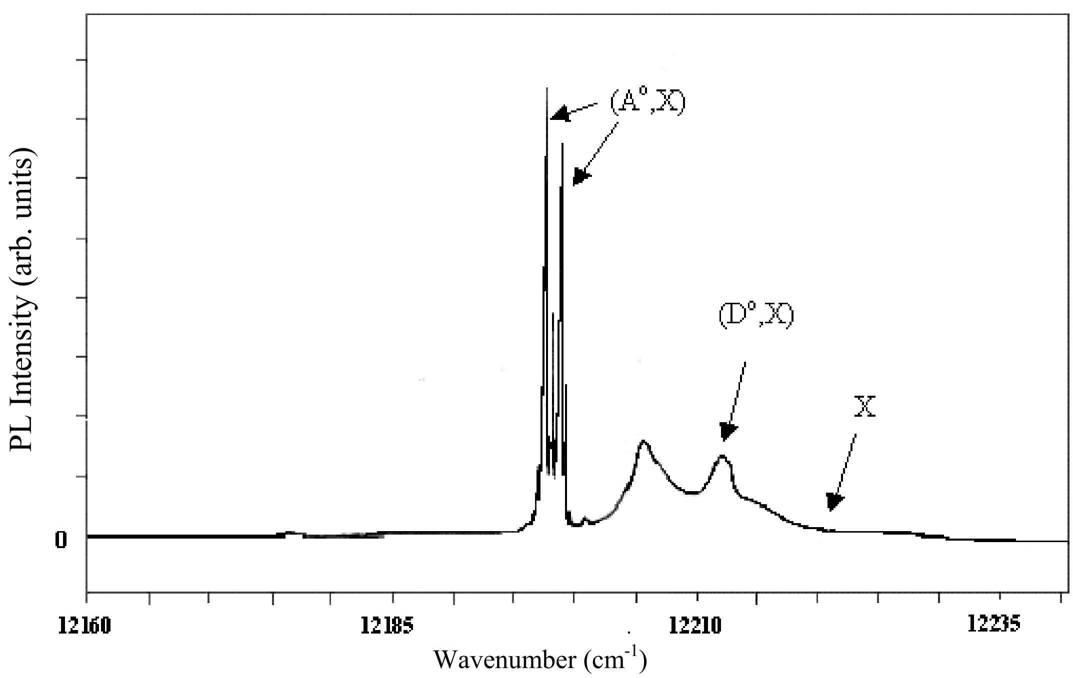

Figure 2: *Photoluminescence spectrum of GaAs epilayer 211SI (Courtesy of M. Thewalt)*

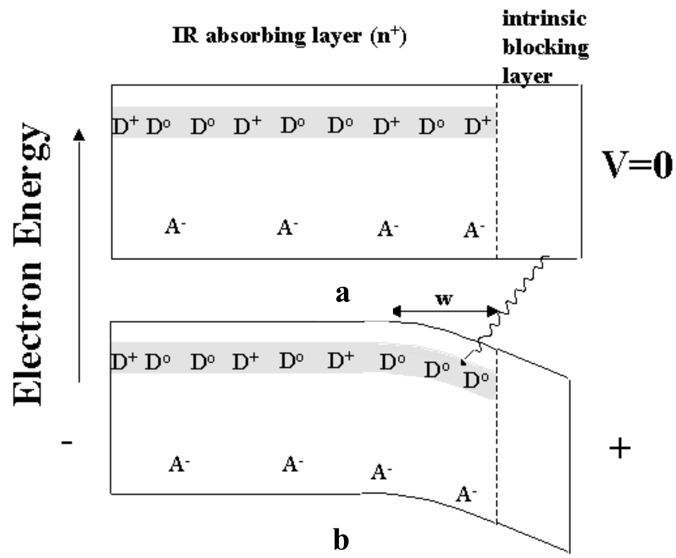

Figure 3: *Band diagram of a BIB* ***a)*** *unbiased* ***b)*** *with an applied bias*

We see that the infrared active region must be *purely doped*, meaning of very low compensation, to have a thick depletion region and hence efficient photon absorption. Growth of such films via liquid phase epitaxy using the dopant tellurium will soon be attempted. Based on the previous success of pure GaAs film growth it is believed that doped layers of sufficiently low compensation for BIB applications can be achieved.

CONCLUSION

GaAs films of extremely high purity have been grown reproducibly via liquid phase epitaxy from Ga solvents. Several samples were characterized using three different techniques, each on different samples. Such films are among the purest ever grown and represent an excellent starting point for the fabrication of GaAs BIB detectors. To reduce the carbon and sulfur contamination in the epilayers further, we will pursue using a crucible made of single crystal sapphire. Such a crucible is beneficial for high-purity GaAs growth because Al is isoelectronic with Ga. Furthermore, a sapphire crucible is expected to absorb fewer volatile impurities from the atmosphere than one made of porous graphite (such as sulfur and oxygen).

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